ARTICLE IN PRESS

Journal of Saudi Chemical Society (2013) **xxx**, xxx–xxx

King Saud University

Journal of Saudi Chemical Society

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ORIGINAL ARTICLE

The fast recovery of gold(III) ions from aqueous solutions using raw date pits: Kinetic, thermodynamic and equilibrium studies

H.M. Al-Saidi *

Department of Chemistry, University College in Al - Jamoum, Umm Al Qura University, Makkah 21955, Saudi Arabia

Received 14 January 2013; accepted 28 June 2013

KEYWORDS

Date pits;
Adsorption;
Gold(III);
Adsorption isotherms;
Kinetic models

Abstract The recovery of Au(III) ions from aqueous solutions employing raw date pits (RDPs) has been systematically investigated in this paper. The morphology, the specific surface area, and the functional groups of RDPs were analyzed using scanning electron microscopy, the methylene blue adsorption method, and FT-IR spectra, respectively. The adsorption of Au(III) onto date pits was achieved quantitatively (90% ± 3.4%) after 90 min of shaking in an aqueous medium containing 0.5 mol L^{-1} HCl. The process of gold(III) ion recovery using RDPs was described by the adsorption coupled reduction mechanism which includes adsorption of Au(III) ions onto RDP surface, followed by the reduction of Au^{3+} to Au. The kinetic data were studied using pseudo-first order, pseudo-second order and intraparticle diffusion models, and was found to follow closely the pseudo-second order model. The batch equilibrium data fitted well to the Freundlich and Langmuir isotherm models, and maximum adsorption capacity of RDPs for Au(III) was 78 ± 1.1 mg g^{-1} at 298 K which was relatively large compared to some adsorbents recently reported. Thermodynamic parameters, namely ΔG, ΔH, and ΔS, showed that the adsorption of Au(III) onto RDPs is exothermic, spontaneous, and chemisorption at low temperature.

1. Introduction

Gold is one of the most important noble metals due to its wide applications in industrial and economic activities. The most common uses of gold are in the industry of jewelry, and electronics (De La Calle et al., 2011). On the other hand, some of the gold(I) compounds have biological activity, which are employed in medicine as anti-inflammatory drugs in the treatment of rheumatoid arthritis (El-Shahawi et al., 2007). Nowadays, the consumption of gold has increased and therefore, the cost of gold production and its price in the market have risen rapidly. However, some wastes such as the waste of electronic equipment (e-waste) contain large amounts of precious metals compared to their own respective ores, and therefore, such wastes may be considered as secondary source of valuable metals. Hence, the development of low cost, and selective

* Tel.: +966 5 04512320; fax: +966 2 5566401.
E-mail addresses: alsaidihm@yahoo.com, hmh1973@hotmail.com.

Peer review under responsibility of King Saud University.

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http://dx.doi.org/10.1016/j.jscs.2013.06.002

technologies for gold ion uptake from industrial effluents is extremely important from economical and environmental points of view, because the recovered ions can be converted into elemental gold. Many methods, such as, co-precipitation (Zhao, 2006), ion exchange (Gomes et al., 2001; Al-Merey et al., 2003; Alguacil et al., 2005), solvent extraction (Kordosky et al., 1992; Akita et al., 1996), and adsorption onto solid – phase materials (Lam et al., 2007; Chang and Chen, 2006) have been used for separation, preconcentration and removal of gold ions from aqueous solutions.

Among these technologies, the adsorption on a solid support has been considered to be a promising technology for the removal and/or recovery of metal ions with the advantages of high efficiency and simple operation (Abidin et al., 2011). The use of activated carbons as adsorbents to remove organic and inorganic materials from aqueous media is widely extended because of their high surface area, microporous characteristic and the chemical nature of their surfaces. However, they are expensive and their regeneration cost is also high. Therefore, several research studies have been focused on the utilization of low cost and naturally available adsorbents e.g. peat mix, garden waste compost, straw, cow manure, coconut chips, chestnut shells, watermelon rinds, charcoal, etc., due to their biodegradability and environmental-friendly properties (El Bakouri et al., 2009).

In recent years, many papers have been published on gold adsorption using various biosorbents (Pangeni et al., 2012; Abidin et al., 2011; Yu et al., 2002; Gamez et al., 2003). However, the literature is still insufficient to cover this research area, and more work and studies are needed in this field to develop other locally available and economical adsorbents.

The date palm may be the world's oldest food-producing plant known to humans. Palm trees are abundant in several countries in the world such as Saudi Arabia, Iraq, Iran, Egypt, Algeria and other Mediterranean countries. Date pits represent about 10% of the date weight (Briones et al., 2011); and therefore any attempt to reutilize this waste will be useful. Raw date pits (RDP) belong to lignocellulosic materials which are mainly composed of cellulose, hemicellulose and lignin, besides other minor components (Briones et al., 2011). Cellulose is a linear polymer with 4-O-β-D-glucopyranose units and insoluble in water, hemicellulose is a low molecular weight chemically ill-defined polysaccharide, so it can be dissolved in water at high temperatures (Briones et al., 2011), while lignin is the most complex natural polymer. It is an amorphous three-dimensional polymer with phenylpropane units that act as a cementing matrix between and within both cellulose and hemicellulose units (Briones et al., 2011). Both cellulose and hemicellulose contain oxygen functional groups e.g. hydroxyl, ether, and carbonyl, and therefore, the presence of such functional groups on the surface of date pits substantially influences on the adsorption mechanism of organic and inorganic compounds on the RDP.

Recent years have seen an upsurge of interest in using the powder of date pits, either in raw form or after chemical and thermal treatment, for the removal of some organic and inorganic pollutants from aqueous media (El Bakouri et al., 2009; Saad et al., 2008; Al-Ghoutia et al., 2010; Banat et al., 2002, 2004). It is worth mentioning that, some natural materials containing oxygen and/or nitrogen functional groups like chitosan and polyurethane foam (PUF) have been effectively used for removal and/or preconcentration of gold(III) species from aqueous solutions (Qu et al., 2009; El-Shahawi et al., 2011a, b). Therefore, RDP, containing the same functional groups, may be a low cost and effective adsorbent for recovery of gold(III) ions from aqueous media. According to my knowledge, there is no previous detailed study about employing RDPs for the removal of Au(III) ions from aqueous media, thus and in continuation to our work on using naturally available adsorbents (El-Shahawi et al., 2011a, b), the present paper would report the salient features of the findings regarding the available functional groups, e.g., hydroxyl and carboxyl groups on RDP and the retention profile of Au(III) onto the RDP as an effective and low-cost solid extractor for the recovery of gold(III) species from aqueous solutions. On the other hand, the most probable adsorption mechanism will also be fully investigated with the aid of different techniques e.g. fourier transform infrared spectroscopy (FT-IR), X-ray diffraction (XRD) and scanning electron microscopy (SEM).

2. Experimental

2.1. Reagents and materials

Deionized water was used throughout. A gold standard solution (1000 mg L^{-1} Au(III) as $HAuCl_4$) in 10% v/v HCl was obtained from (Prolabo, Leicestershire, England). More diluted standard solutions were then prepared by dilution. Hydrochloric acid (Aldrich, $d = 1.19$ g mL^{-1} and 37%) was used to adjust the acidity of aqueous gold solution. A series of Britton–Robinson buffer solutions of pH 1.8–12.2 were prepared by mixing equimolar concentrations (0.4 mol L^{-1}) of the acid mixture: boric, acetic and phosphoric acids in deionized water and adjusting the pH of the solution to the required value with NaOH (Vogel, 1980).

2.2. Apparatus

A Perkin–Elmer (AAnalyst 700, USA) atomic absorption spectrometer equipped with deuterium background corrector and hollow-cathode lamp operated at 242.8 nm with a 0.7 nm slit width was used for gold determination in aqueous solutions. All measurements were carried out in an air–acetylene flame. Other instrumental parameters were adjusted according to the manufacturer's recommendations. IR (400–4000 cm^{-1}) spectra were recorded on Shimadzu FT-IR 8400 spectrophotometer using KBr disk. Carbon, hydrogen, nitrogen and sulfur content in the RDP were determined by a Perkin–Elmer 2400 C series elemental analyzer, USA. A mechanical shaker (Corporation Precision Scientific, Chicago, USA) with a shaking rate in the range 10–250 rpm was used in batch mode. A Thermo Fisher Scientific Orion model 720 pH Meter (Milford, MA, USA) was used for pH measurements.

2.3. Preparation of raw date pits

The RDPs selected for the present work were collected from the date palm grown in El-Qassim region (Khalas), Saudi Arabia. The collected date pits were kept at ambient temperature in the laboratory for a week and then dried at 70 °C for one day in the drying oven before crushing them in an electric